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Title of the Invention:

Electrochromic Display Device

CLAIM

An electrochromic display device comprising a display substrate having display electrodes, an opposing substrate having an opposing electrode, and a liquid electrolyte confined between said two substrates as it has an electrochromic material and a support electrolyte dissolved therein, characterized in that said electrochromic material consists of a mixture of an oxidation-luminescence type electrochromic material and a reduction-luminescence type electrochromic material which will develop the same color.

SPECIFICATION

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Detailed Description of the Invention

The present invention relates to an electrochromic display device (ECD) and, more particularly, to an ECD capable of achieving high contrast.

The ECD of the present invention is of a dissolution/diffusion type that utilizes the phenomenon that an electrochromic (EC) material in a liquid electrolyte undergoes an oxidation-reduction reaction based on an electrode reaction, thereby experiencing reversible color formation and erasure. ECDs are drawing increasing attention because they can be operated at low voltage and power and yet provide a bright and sharp display.

A conventional most representative ECD of a dissolution type is shown schematically in the accompanying drawing. A display substrate 1 is combined with an opposing substrate 2 via a spacer 7 and sealed with sealing members 8 to form a

cell, which is injected with a liquid electrolyte 6. To provide a white background, a light reflecting plate is provided between the two substrates or, alternatively, the liquid electrolyte is mixed with a white powder to make a paste. The light reflecting plate is made of a ceramic material such as alumina or a high polymer. The white powder to be mixed with the liquid electrolyte is the powder of titanium oxide, alumina, etc.

The reflecting plate and the white powder are hereunder collectively referred to as a "light reflector".

The display substrate 1 is typically a transparent substrate made of glass, plastics, etc. The display substrate 1 is overlaid with display electrodes 3. The display electrodes 3 are transparent electrodes in the form of a tin oxide (SnO_2) film, an indium oxide-tin oxide (ITO) film, etc. They are typically formed by vacuum evaporation but chemical methods such as spraying may also be employed. While the opposing substrate 2 with an opposing electrode 4 may be of various designs, the following are representative: a glass substrate overlaid with a transparent electrode; a glass substrate overlaid with a metal film; a glass substrate overlaid with a pressed mixture of an iron complex and carbon; and a metal plate.

While various methods can be used to display numerals, letters, etc., one of them is to provide surface masks 5 in such a way that the transparent electrode 3 is exposed to the liquid electrolyte only in the areas corresponding to the patterned segments to be displayed. The surface masks are

commonly made of a white ink comprising the particles of a white powder dispersed in a resin and it is formed by screen printing. If the segments are to be displayed separately, the display electrode to which they are attached have to be divided accordingly. It should be noted that the surface masks 5 shown in the drawing are by no means essential.

The liquid electrolyte 6 is composed of a solvent, a support electrolyte and an EC material. The solvent may be of any type that has great polarity and which is stable. In addition to water, non-aqueous solvents such as propylene carbonate and dimethylformamide may be used. The following description is chiefly concerned with the case of using a non-aqueous solvent. The support electrolyte is a common inorganic salt if water is used as the solvent; if a non-aqueous solvent is used, the support electrolyte is selected from salts of alkali metals or tetraalkylammonium with halogen perchlorate (ClO_4), fluoroborate (BF_4) and fluorophosphate (PF_5). The EC material is selected from among inorganic materials such as salts of transition metal compounds exemplified by Na_2WO_4, $CaWO_4$, $BaWO_4$ and Na_2MoO_4, organic materials including aromatic or heterocyclic compounds such as viologen, tetrathiafulvalene, pyrazoline, fluorene, anthraquinone, pyrylium, pyridium and Methylene Blue, as well as derivatives thereof, and organometallic materials such as ferroin and ferrocene.

The conventional dissolution-type ECD having the above-described structure is capable of displaying only one color. For example, an ECD using butyl anthraquinone as an EC

matarial provides white in the initial state and turns red when a negative voltage is applied to the transparent electrode and reverts to the initial white upon application of a reverse voltage. The white color is characteristic of a light scatterer.

With an ECD of this conventional construction, a 2:1 contrast is the highest white contrast that can be realized in practice. The reason for this limited contrast is that only the color development from the electrode on one side is utilized.

It is therefore an object of the present invention to provide an electrochromic display device capable of high contrast.

According to the invention, there is provided an electrochromic display device comprising a display substrate having display electrodes, an opposing substrate having an opposing electrode, and a liquid electrolyte confined between said two substrates as it has an electrochromic material and a support electrolyte dissolved therein, characterized in that said electrochromic material consists of a mixture of an oxidation-luminescence type electrochromic material and a reduction-luminescence type electrochromic material which will develop the same color.

The electrochromic display device of the invention has the same construction as the illustrated conventional ECD of a dissolution type, except that it should not have any light reflector. A characterizing feature of the invention is to use a mixture of an oxidation-luminescence type (O-type) EC

material and a reduction-luminescence type (R-type) EC material. An O-type EC material is nearly colorless under a neutral condition and develops color when oxidized. An R-type EC material is also nearly colorless under a neutral condition but develops color when reduced.

While the opposing electrode 4 and the opposing substrate 2 may basically be formed of the materials already described herein, particularly good display characteristics can be provided by using the following materials. For example, the opposing electrode 4 may be the transparent electrode already described herein and the opposing substrate 2 may be a glass plate in a thickness of about 0.5 mm. If a white plate such as a sheet of white paper, an aluminum plate or a white synthetic resin plate is placed in contact with the opposing substrate 2, an ECD is obtained that has a shadowless white background. In another method, a transparent electrode may be used as the opposing electrode 4 whereas a white substrate such as an alumina substrate is used as the opposing substrate 2; this is also effective in providing an ECD having a shadowless white background.

The operating mechanism of the ECD of the invention will now be described. The operation starts with application of an external voltage to the display electrodes 3 and the opposing electrode 4. The O-type EC material develops color at the electrode or electrodes supplied with a positive voltage, whereas the R-type EC material develops color at the electrode or electrodes supplied with a negative voltage. In the ECD of the invention, both the O- and R-type EC materials develop the

same color and the developed color can be seen from the display substrate irrespective of which type of EC material has developed that color. As a result, a high-contrast display of the same color can be produced regardless of the polarity of the applied voltage. If voltage application is turned off (the applied voltage is zero volts), the O- and R-type EC materials which have developed color will react with each other and revert to a neutral state. In other words, the display disappears and the state within the liquid electrolyte will revert to the initial.

While the basic method of voltage application to the ECD of the invention is as described above, the ECD fabricated in each of the Examples that follow has a threshold for color development at about 1.0 V, so rapid response can be realized if a voltage sufficiently higher than 1.0 V (typically about 2.0 V) is applied to develop color while a voltage slightly lower than 1.0 V (typically about 0.8 V) is applied to erase the color.

An ECD of a dissolution type that uses both an O-type EC material and an R-type EC material but which does not use any light reflector is already disclosed in Japanese Patent Application No. 145767/1977 and Japanese Patent Public Disclosure No. 31297/1979. However, those EC materials do not develop the same color and the displayed color is a mixture of two colors. Therefore, the ECDs disclosed in those patents will display a dull and rather contaminated color. On the other hand, the ECD of the invention which employs EC materials capable of developing the same color can provide a

color of higher purity and, hence, a sharp display.

While the following description concerns only the display of blue color, it should be noted that the invention is also applicable to the display of other colors. For display of blue color, furyl and benz[a]anthracene-7,12-dione (hereunder abbreviated as B-a-AQ) may be used as R-type dyes, whereas 2-aminofluorenone (hereunder abbreviated as FN-1) and 1-p-phenyl-3-p-diethylaminostyryl-5-diethylaminophenyl-Δ^2-pyrazoline (hereunder PZL-B) may be used as O-type dyes.

The following examples are provided for the purpose of further illustrating the invention.

Example 1

The drawing shows typical ECD for use in implementing the invention.

Display substrate 1 and opposing substrate 2 were both made of glass but in different thicknesses of 1.0 mm and 0.3 mm. Display electrodes 3 and opposing electrode 4 were both an indium oxide/tin oxide (ITO) electrode, which was formed by vacuum evaporation. Spacer 7 was made of a very thin Tetron sheet that separated the two substrates by a distance of 30 µm which, in turn, were sealed with an epoxy adhesive. A liquid electrolyte was prepared from the following formulation: B-a-AQ as R-type EC material (0.2 mol/L); PZL-B as O-type EC material (0.2 mol/L); TBAI as electrolyte (0.3 mol/L); and N-2-methylpyrrolidinone (hereunder abbreviated as NMP) as solvent. A sheet of white paper was placed at the back of the opposing electrode 2 to provide a reflector plate. The thus fabricated ECD displayed white color in the initial state.

When the transparent electrodes were supplied with a voltage of -2.0 V that was negative to the opposing electrode, a sharp display with 7:1 contrast was provided within a response time of 0.1 second. The color disappeared in 0.2 seconds after the application of zero volts. When the erase voltage was increased to +0.8 V, the erase time could be shortened to 0.1 second. Even when the polarities were reversed (first +2.0 V then -0.8 V, was applied), EC characteristics of the same contrast and same response time were attained.

Example 2

An ECD of the same construction as in Example 1 was fabricated from the same materials as used in Example 1, except that an alumina substrate in a thickness of 1 mm was used as the opposing substrate 2. In Example 2, no sheet of paper was necessary at the back of the opposing substrate 2. The drive conditions and the display characteristics were the same as in Example 1.

Example 3

An ECD of the same construction as in Example 1 was fabricated from the same materials as used in Example 1, except that furyl was used as R-type EC material whereas FN-1 was used as O-type EC material. The drive conditions and the display characteristics were the same as in Example 1.

It should be noted that the O-type and R-type EC materials that can be used in the invention are in no way limited to the examples described herein and any EC materials can be used if they develop the same color upon oxidation or

reduction. By using a wide variety of O-type and R-type EC materials in the ECD of the invention, various color displays can be realized in high contrast.

Brief Description of the Drawing

The drawing is a sectional view of a typical ECD design.

1 ... display substrate
2 ... opposing substrate
3 ... display electrode
4 ... opposing electrode
5 ... surface mask
6 ... liquid electrolyte
7 ... spacer
8 ... sealant

に記したEC材に限定されず、酸化又は還元で同じ色に発色するEC材は、いかなるものも用いることができる。このような種々のO型EC材、R型EC材とを本発明のECDに用いることにより、種々の色の高コントラストの表示が実現される。

図面の簡単な説明

図は、一般的なECDの構造を示す断面図を示す。

図について、

1. 表示基板　　2. 対向基板
3. 表示電極　　4. 対向電極
5. 表面マスク　　6. 電解液
7. スペーサ　　8. シール材

である。